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REVISION

6th September 2016

**Reagent-less Electrochemiluminescence (ECL) from a
Nanoparticulate Polymer of Intrinsic Microporosity
(PIM-1) Immobilised onto Tin-Doped Indium Oxide (ITO)**

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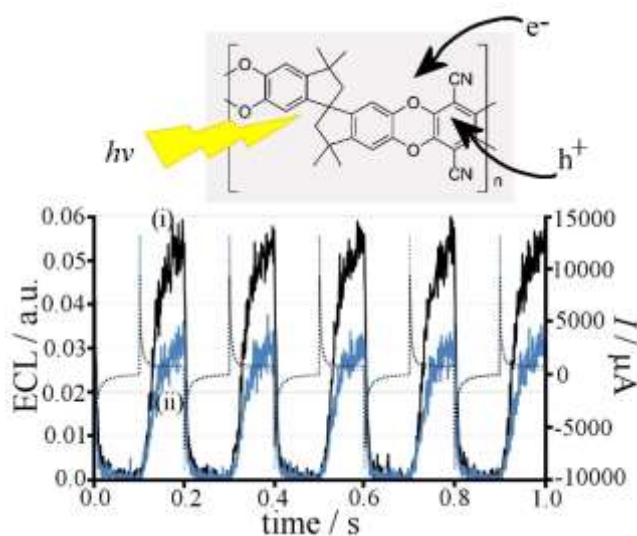
To be submitted to CHEMELECTROCHEM (special issue for Christian Amatore)

Proofs to F. Marken (f.marken@bath.ac.uk)

Abstract

In contrast to most common electrochemiluminescence (ECL) techniques that require either an additional reagent or continuous pulsing between oxidative and reductive potentials, here a fluorescent Polymer of Intrinsic Microporosity (PIM-1) is shown to exhibit intrinsic ECL without the need for a co-reactant, at positive applied potentials and as a function of pH. PIM-1 is known to possess high microporosity (based on its rigid and contorted molecular structure) and excellent fluorescence properties. By depositing a nanoparticulate form of PIM-1 material onto tin-doped indium oxide (ITO), we achieve a hierarchically porous deposit with good sustained electro-chemiluminescence activity in aqueous media. The mechanism for this reagent-less electrochemiluminescence is suggested to be linked to reactive oxygen species produced at positive potentials and discussed in terms of potential analytical applications.

Keywords: membrane; polymer nanoparticle; light emission; reactive oxygen; sensor.



Graphical abstract:

1. Introduction

Electrochemiluminescence (ECL), which first began to be investigated in detail in the 1960's,^[1,2,3] today is used as the basis for a range of highly sensitive detection methods.^[4,5,6,7] ECL occurs when, following its electrolysis, a molecular emitter is activated into an emissive excited state via a homogeneous electron transfer between it and another electrogenerated species. If the excited state is generated by reaction between the emitter and a species formed by oxidation or reduction of a sacrificial reagent, this is known as “co-reactant ECL”. When the excited state is formed by sequentially generating the oxidised and reduced form of the emitter itself, this is known as “annihilation ECL”. Typically, the emitter is either recycled (e.g. for $\text{Ru}(\text{bipy})_3^{2+}$ with bipy = bipyridyl) or consumed (e.g. for luminol). Instrumentation for the ECL has evolved and can now be low cost and mobile.^[8,9] Applications have been developed in the areas of biosensing,^[10] microfluidic detection,^[11] detection of drugs,^[12] or as cytosensors.^[13] Traditionally, $\text{Ru}(\text{bipy})_3^{2+}$ has been the predominant ECL emitter (the proto-typical ECL system introduced by Bard and co-workers^[14,15]), but more recently a much wider range of materials including carbon nano-dots have been reported to give ECL emission^[16] and nano-particle enhanced ECL has been developed.^[17,18] Low cost organic emitters of ECL are of considerable interest^[19] and novel ECL-dendrimers^[20] or polymeric systems with imprinted “recognition” and with ECL read-out^[21] have been described.

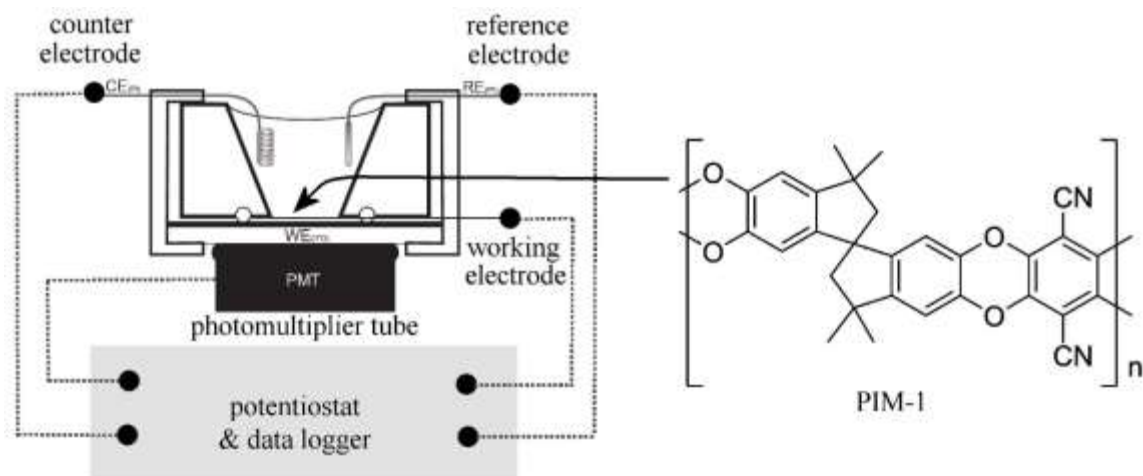


Figure 1. Schematic drawing of the electrochemical cell with a transparent ITO working electrode for generation of ECL emission into the photomultiplier tube, which is connected to the data input of the potentiostat. The molecular structure of the PIM-1 ECL emitter is shown on the right.

Polymers of Intrinsic Microporosity (PIMs) have emerged^[22] as highly processible and useful microporous materials with applications in gas absorption,^[23] catalysis,^[24] and gas separation.^[25] More recently, promising liquid phase applications, particular in electrochemistry, have been proposed.^[26] For example, PIM-EA-TB material has been shown to protect fuel cell catalysts,^[27] to allow molecular catalysts to be heterogenised,^[28] and to give “ionic diode” and desalination functionality in membranes.^[29]

Here, we present a novel organic ECL material based on a particular Polymer of Intrinsic Microporosity (PIM-1), which demonstrates pH dependent ECL emission without the need either for additional reagents or oxidative-reductive potential cycling. In future, this novel PIM-ECL emitter could be very useful, for example in microfluidic systems, as electro-

luminescent nanoparticles, or for *in situ* detection applications including the detection of reactive oxygen species.

2. Experimental

2.1. Chemical Reagents. Polymer PIM-1 was prepared following a literature procedure.^[30,31] Chloroform, methanol, 30% H₂O₂, Na₂(CO₂)₂, NaOH, and phosphoric acid (85 %) were obtained from Aldrich or Fisher Scientific and used without further purification. Solutions were prepared with filtered/deionised water of resistivity 18.2 MΩ cm from a Thermo Fisher filter system.

2.2. Instrumentation and Procedures. Current and ECL transients were simultaneously recorded using a μAutolab type III potentiostat (Ecochemie, NL) controlled by GPES software and coupled with a photo-multiplier tube (PMT, PMM02, Thorlabs UK) held at 800 V accelerator voltage using a programmable function generator (TTi, TG1304, Thurlby Thandar Instruments Ltd). The photocurrent produced at the PMT was converted to a voltage signal and fed into the external input channel of the Autolab. A three electrode system was used in a homemade electrochemical cell. The working electrode was a modified tin-doped indium oxide (ITO) electrode. Platinum wires were used as counter and quasi reference electrode. ITO was cut to size for the electrochemical cell and modified with commercial ITO nanoparticles^[32] (diameter ca. 20 nm, dispersion in water, Nanophase Technologies Corp. USA) in order to increase the contact and adhesion with the PIM-1 nanoparticles. Scanning electron microscopy images were obtained on a JEOL JSM6310 SEM and transmission electron microscopy images were obtained on a JEOL-2010 TEM.

2.3. Synthesis of PIM-1 Nanoparticles. PIM-1 nanoparticles were synthesized using the re-precipitation method. A volume of 2 cm³ of PIM-1 polymer dissolved in chloroform (1 mg cm⁻³) was added drop-wise into 20 cm³ of methanol under vigorous stirring at room temperature. The mixture was stirred for 12 hours and then centrifuged for 30 min at 5000 rpm. Excess methanol was removed to give 0.5 cm³ and the PIM-1 nanoparticles were re-dispersed by ultrasonication. Typically, 15 μ L of this 4 mg cm⁻³ PIM-1 nanoparticle dispersion is then deposited onto an area of approximately 2 cm² on the ITO electrode to give approximately 30 μ g cm⁻². Figure 2 shows scanning electron micrographs for (A) bare ITO, (B) ITO nanoparticles on ITO, and (C) PIM-1 nanoparticles on ITO. The transmission electron micrograph in Figure 2D reveals a network-like relatively open morphology.

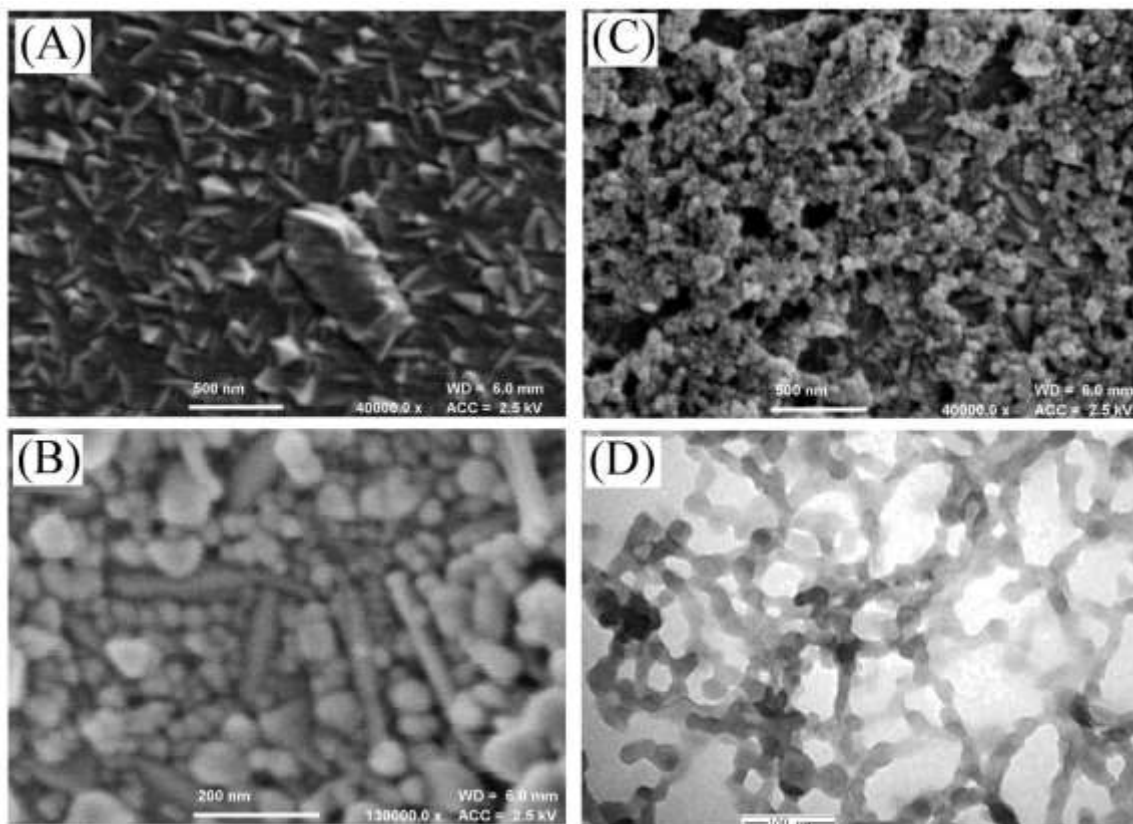


Figure 2. Scanning electron optical images for (A) base tin-doped indium oxide (ITO), (B) ITO nanoparticles on ITO, and (C) PIM-1 nanoparticles ($30 \mu\text{g cm}^{-2}$) on ITO. (D) Transmission electron micrograph showing a network of PIM-1 nanoparticles.

3. Results and Discussion

3.1. PIM-1 Electrochemiluminescence I. Effect of Electrolyte. Initial experiments, where PIM-1 was simply drop-cast as a film onto the ITO working electrode showed only weak ECL emission upon scanning the applied potential positive and oxidation of the film or electrolyte. In order to improve reproducibility and luminosity, the PIM-1 material was then converted into nanoparticles of approximately 20 nm diameter (see experimental; Figure 2D) and deposited onto a layer of ITO nanoparticles (employed to improve adhesion and increase active surface area). The resulting electrode produced higher ECL emissions

in both aqueous 0.01 M NaOH and aqueous phosphate buffer pH 12 (see Figure 3), the onset of which coincided with that of the anodic current at 1.4 V vs. Pt. Perhaps surprisingly, the ECL emission was generated without direct reduction of the film and in the absence of any co-reactants such as electron donating amines or oxalate. Additional experiments performed under exactly the same conditions but in the absence of PIM-1 nanoparticles did not result in ECL emission. This suggests that PIM-1, which is highly fluorescent in nature, is the emitter.

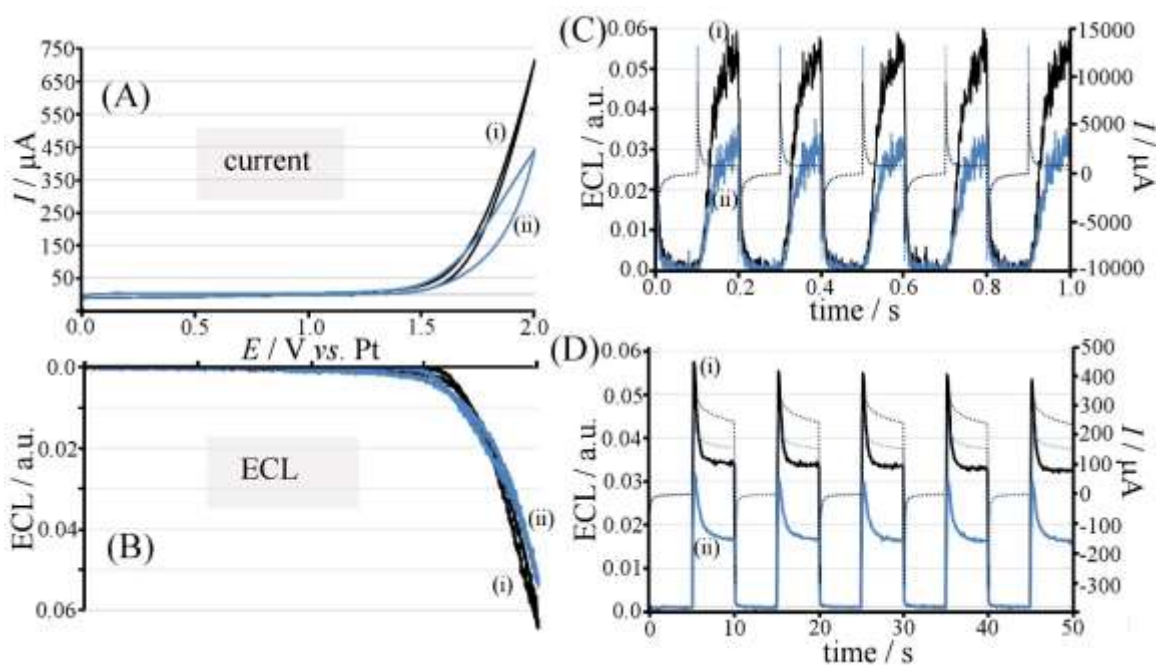


Figure 3. (A) Cyclic voltammograms (11th potential cycle shown, scan rate 0.2 Vs⁻¹) for a PIM-1 nanoparticle coated ITO/ITO electrode immersed in (i) 0.01 M aqueous NaOH solution and (ii) 0.01 M phosphate buffer pH 12. (B) Simultaneously recorded ECL data. (C) Chronoamperometry (dotted lines) and chronoluminometry (solid lines) (switching between 0.05 s 0.0 V and 0.05 s 2.0 V) in (i) 0.01 M aqueous NaOH solution and (ii) 0.1 M phosphate buffer pH 12. (D) Chronoamperometry (dotted lines) and chronoluminometry (solid lines) (switching between 5 s 0.0 V and 5 s 2.0 V).

In the first 10 potential cycles the ECL signal gradually increases and stabilised, and following on from this a stable ECL emission was detected for a prolonged time of use with only slow decay of the signal. When going to higher potentials (3 V vs. Pt) the emission is further enhanced, but the signal decay is more pronounced. The loss of emission signal at higher potentials is likely to be a sign of PIM-1 consumption during ECL. Data in Figure 3A and 3B demonstrate that very similar characteristics are observed in 0.01 M NaOH or in phosphate buffer at pH 12. Chronoamperometry data in Figure 3C and 3D show that a rapid rise in ECL signal within 100 ms is followed by a slower decay within 5 s to result in a more constant phase of light emission.

3.2. PIM-1 Electrochemiluminescence II. Effect of pH. When investigating the effect of the pH, first an increase in ECL with pH is observed and then a clear detrimental effect of further increasing the concentration of aqueous NaOH is seen (Figure 4A and 4B). Although the current signal for the modified electrode is increased, the ECL output is decreased, which is ascribed here predominantly to the effect of pH.

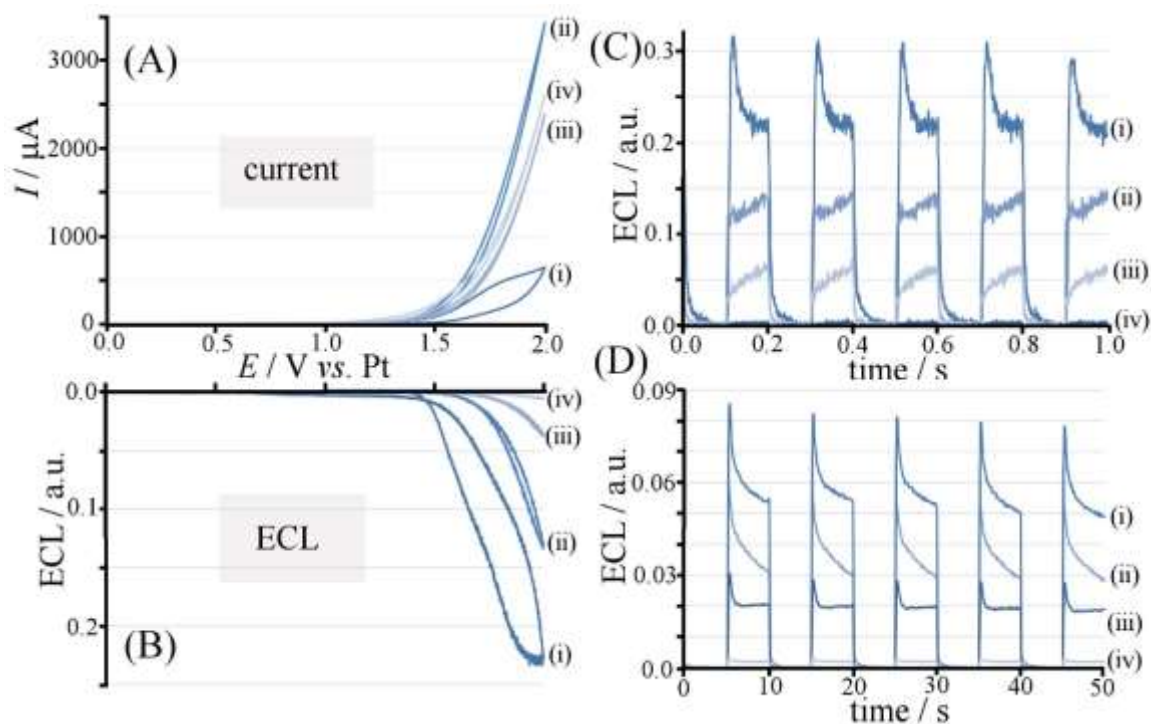
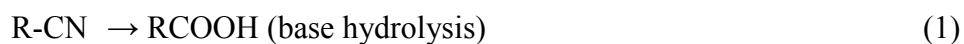


Figure 4. (A) Cyclic voltammograms (scan rate 0.2 Vs^{-1}) for a PIM-1 nanoparticle coated ITO/ITO electrode immersed in aqueous NaOH solution (i) 0.01 M, (ii) 0.02 M, (iii) 0.2 M, and (iv) 0.5 M. (B) Simultaneously recorded ECL data. (C) Chronoluminometry (0.5 s 0.0 V and 0.5 s 2.0 V) in aqueous NaOH solution (i) 0.01 M, (ii) 0.02 M, (iii) 0.2 M, and (iv) 0.5 M. (D) Chronoluminometry (5 s 0.0 V and 5 s 2.0 V).

When going to more acidic pH conditions in aqueous phosphate buffer (Figure 5A and 5B), the ECL intensity is systematically decreased. At pH 5 only a relatively low level of remaining emission is detected. The molecular structure of PIM-1 (see Figure 1) shows no obvious sites for protonation or deprotonation (note: it is possible that both nitrile and the ether groups could be protonated and disrupt fluorescence) to explain these trends in the studied range of aqueous pH values. However, it is possible that alkaline conditions facilitate the formation of reactive oxygen species at the ITO electrode surface, which could then react/transfer holes within the microporous PIM-1. Furthermore, it is known that the $-\text{CN}$ groups can be base-hydrolysed to $-\text{COOH}$ functional groups.^[33] Such organic

acids are then likely to (i) cause the pH-dependent ECL activity and (ii) explain the ECL emission mechanism as based on a process in which a strongly reducing species RCOO^\bullet or R^\bullet is generated *in situ* according to reactions 1-5 below, (similar to the mechanisms reported for the chemiluminescence of organic acids such as pyruvate and oxalate with $\text{Ru}(\text{bipy})_3^{3+}$).^[34,35]



Here R is a portion of the polymeric species and L^+ is the PIM-1 luminescent moiety containing a hole. The formation of the hole (in equation 3) close to the surface of the ITO electrode surface is likely to occur here either directly or indirectly via reactive oxygen intermediates. More work will be needed to unravel further details for this mechanism.

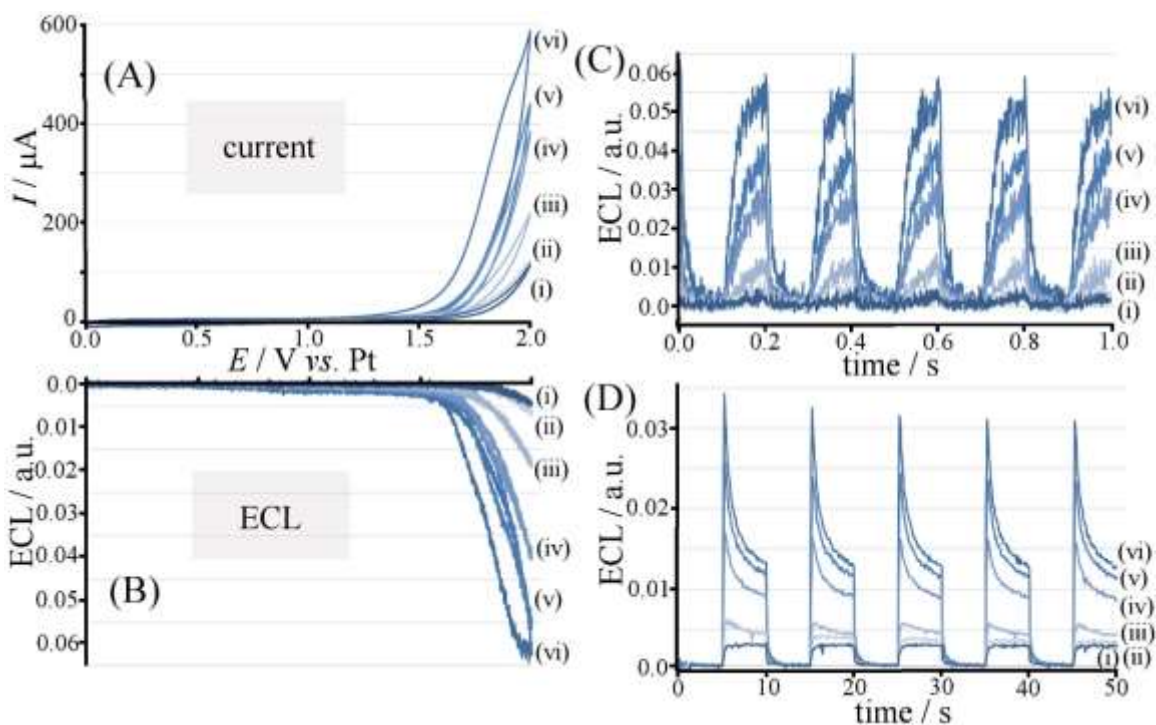


Figure 5. (A) Cyclic voltammograms (scan rate 0.2 Vs^{-1}) for a PIM-1 nanoparticle coated ITO/ITO electrode immersed in 10 mM phosphate buffer solution (i) pH 5, (ii) pH 6, (iii) pH 7, (iv) pH 8, (v) pH 9, and (vi) pH 10. (B) Simultaneously recorded ECL data. (C) Chronoluminometry (switching between 0.05 s 0.0 V and 0.05 s 2.0 V) in 10 mM phosphate buffer solution (i) pH 5, (ii) pH 6, (iii) pH 7, (iv) pH 8, (v) pH 9, and (vi) pH 10. (D) Chronoluminometry (switching between 5 s 0.0 V and 5 s 2.0 V).

3.3. PIM-1 Electrochemiluminescence III. Effect of Oxalate. In order to verify the possible ECL-enhancing effect of oxalate based on the mechanism suggested in equations 1 to 5, additional experiments were performed both for 10 mM NaOH and for 10 mM phosphate buffer pH 12 media. When working in a potential range up to 2 V vs. Pt, addition of 10 mM di-sodium oxalate did generally not significantly affect the light emission. When working in phosphate buffer pH 12 and scanning the potential more positive to 4 V vs. Pt, oxalate again did not cause significant changes. However, in 10 mM NaOH and when

scanning the applied voltage to 4 V vs. Pt (see Figure 6), a clear increase in ECL signal is observed. Over three consecutive potential cycles the current in the presence of 10 mM oxalate is tripled when compared to data obtained in the absence of oxalate. At the same time the ECL signal also triples relative to that obtained in the absence of oxalate. However, also a rapid decay of the ECL response is observed. These results suggest that (i) phosphate is able to suppress uptake of oxalate into PIM-1 and (ii) oxalate can further enhance the ECL mechanism (see equations 3 to 5), although only under extreme conditions. In future, further work will be required and in particular spectra for the ECL emission will have to be recorded to gain further insight into the mechanism.

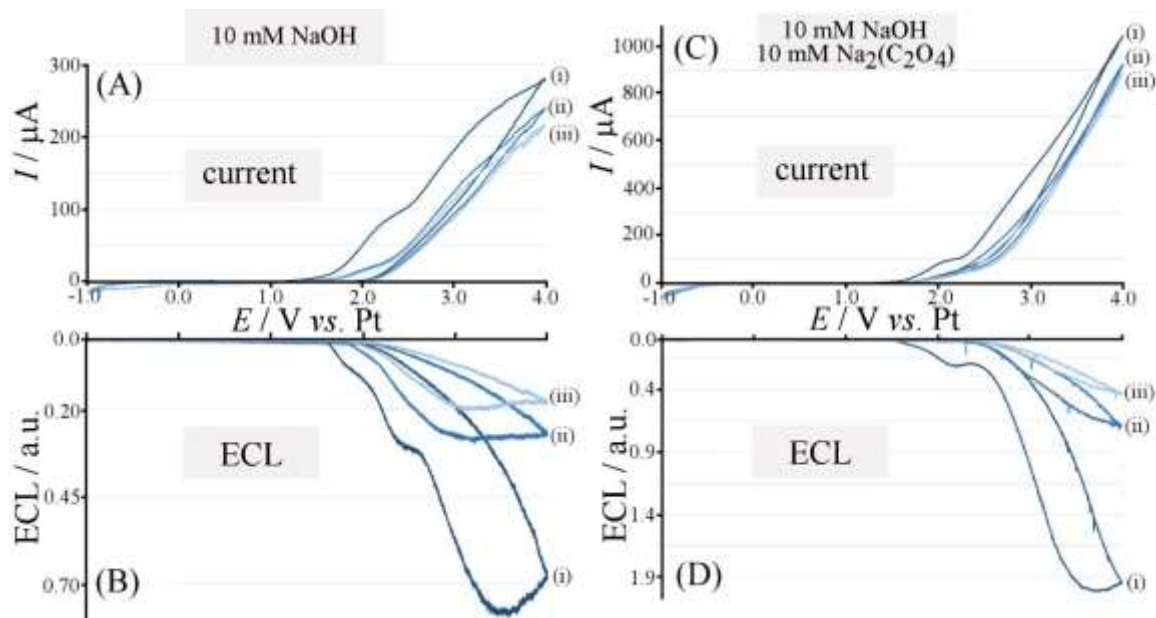


Figure 6. (A) Cyclic voltammograms (scan rate 0.2 Vs^{-1} ; (i) to (iii) show consecutive potential scans 1 to 3) for a PIM-1 nanoparticle coated ITO/ITO electrode immersed in 10 mM NaOH for an enlarged potential window. (B) Simultaneously recorded ECL data. (C) As above, but in 10 mM NaOH and 10 mM $\text{Na}_2(\text{C}_2\text{O}_4)$. (D) Simultaneously recorded ECL data.

4. Conclusion

Preliminary data for a novel reagent-less electrochemiluminescence system are reported. The microporous polymer PIM-1 is shown to emit light on ITO substrates under conditions of positive applied potential and the presence of weakly acidic or basic conditions ($\text{pH} > 5$). The ability of PIM-1 to give reagent-less pH dependent ECL may be of considerable benefit in analytical applications such as assays based on enzyme substrate reactions involving protonation/deprotonation steps. Further work will be required to also explore the ability of PIM-1 to exhibit reagent-less chemiluminescence, for example when impregnated with metal catalyst and exposed to reactive oxygen species or peroxides. Replacing the electrode with a purely chemical mechanism will substantially broaden the potential for analytical applications in reagent-less chemiluminescence. In future, custom-made microporous PIM materials could be designed to combine into one material all the molecular components necessary for hole and electron generation as well as the luminophore for the light emission.

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